

The Allowable Temperature and Relative Humidity Range for the Safe Use and Storage of Photographic Materials

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Abstract:

The temperature and relative humidity tolerance of conventional photographic materials is discussed in this paper, and recommendations for their safe use and storage are presented. The physical stability, chemical stability, moisture buffering performance, and the importance of the glass transition temperature of gelatin are explained. The logic behind the storage recommendations is given, and a set of graphs shows the allowed and disallowed combinations of temperature and relative humidity. The combined effects of storage and use on overall chemical stability are also illustrated using "Time-out-of Storage" tables.

Introduction:

Conventional photographic materials typically make use of a gelatin binder in one or more coating layers. Although the final image may be formed by silver particles, organic dyes, or other inorganic components, gelatin has been the material of choice for more than a century to serve as the image binder. Additional gelatin layers are also frequently present. They function, for example, as anti-curl layers or overcoat layers which improve abrasion resistance and/or alter surface texture. The gelatin layers are adhered to a common support layer, and substrates made of cellulose esters (e.g., acetate), polyester, glass, paper, or polyethylene resin coated paper have found widespread usage. The physical structure of the majority of 20th century photographic films and prints can be understood by considering combinations of these basic material components. The environmental guidelines for safe use and storage of photographic materials presented in this paper are applicable to and inclusive of these common varieties of films and papers.

Temperature and relative humidity recommendations for photographic materials should be cited with two purposes in mind -- safe storage and safe use. Room temperature and moderate humidity ranges are more suited to the requirements of frequent access and comfortable use and display while low temperature storage is important, indeed necessary in most cases, to meet long-term preservation objectives. Only temperature and humidity levels that reasonably guarantee both chemical and physical safety can be allowed, and the materials must not be harmed by cyclical conditions which occur as they move between storage and use.

Chemical stability is often determined by accelerated aging tests, and natural aging has confirmed how photographic materials degrade over time. The physical stability of photographic images has been more difficult to quantify. Anecdotal evidence clearly indicates that wide environmental cycles, notably changes in relative humidity, cause physical damage to photographs. The damage appears as cracks, flaking, and permanent warpage or curl. Just as chemical stability data indicate an allowable range, physical stability must also be ensured by limiting the changes in temperature and relative humidity to an allowable range. A threshold

under which minimal physical damage to museum objects will occur has previously been suggested but not determined.¹ Cautious experts have therefore advised against repetitive temperature and relative humidity cycles of any magnitude. Most photographic storage specifications have likewise been established with very tight tolerances for environmental cycling, as tight as modern HVAC systems can control (typically $\pm 1^{\circ}\text{C}$ and $\pm 2\% \text{ RH}$).

Unfortunately, specifications with narrow tolerances are difficult to maintain and make the frequency of access versus the physical well-being of the collection a problematic issue. One cannot freely move items to and from storage and display environments without violating the tight environmental tolerances unless the storage and user environments are perfectly matched. This is very often not the case, particularly when cool and cold storage climates are used. The situation leads to uncertainty for the collection manager. How many times a day, a month, or a year can one violate the temperature and humidity tolerances? How many large environmental fluctuations equate to more frequent but smaller fluctuations? Ironically, what if a safe threshold really does exist under which no physical damage occurs in response to changes in temperature and relative humidity? These questions required new research and a scientific method for their resolution.²⁻¹⁶

The Yield Point as a Criterion for Physical Damage:

Materials do indeed have a threshold for damage as well as a reversible range of elasticity. As long as the materials are not subjected to environmental cycles which cause them to exceed their true yield point, the materials behave elastically. The materials will expand and contract in response to temperature and RH fluctuations in a completely reversible manner. No permanent plastic deformation or fracture occurs. Plastic deformation leads to micro defects such as dislocations and voids which ultimately cause cracks, and delamination of composite layers. Many materials tolerate extensive amounts of plastic deformation before actually breaking. However, very brittle materials have little ability to plastically deform before fracture occurs. Total physical safety for all material components can therefore only be guaranteed when all materials remain elastic and are not taken beyond their yield point.

Many tests have been conducted in our laboratory in order to determine the true yield point of a wide variety of cultural materials. The yield point may be viewed as the change in length which must be exceeded in order to cause a permanent change in length of the material. The yield point therefore defines the limits of expansion or contraction which are fully reversible. The test materials have included gelatin, polyester, cellulose, cellulose acetate, cellulose nitrate, hide glues, oil, alkyd and acrylic paints, natural and synthetic varnishes, metals, woods, hair, epoxies, and many others old and new. A surprising result was that the true yield point is very consistent. Materials yield at approximately 0.4% elongation (or slightly greater if they have experienced strain hardening). By using the conservative value of 0.4% elongation for yield and with knowledge of thermal and humidity coefficients of expansion, the temperature and RH changes necessary to reach the yield point can be conservatively estimated. The worst case resulting from environmental changes occurs when a material is fully restrained from movement in a uniaxial direction. Physical restraint occurs by confining materials in

frames or other fixtures and also arises when one material is bonded to other materials which possess different coefficients of expansion. The composite layers of a photograph are an excellent example of the latter case. A gelatin emulsion adhered to glass, for example, will try to shrink in response to a decrease in relative humidity, but it is prevented from doing so by the glass substrate which remains rigid and unresponsive to the change in humidity. Thus, restraining a layer so that it is not free to shrink or expand in response to environmental changes induces stresses that are just like mechanically applied stresses.^{2,3} In other words, stresses caused by changes in temperature and relative humidity have the same effect on an object as mechanical stresses caused by physical handling (e.g., bending, stretching, etc.). With this knowledge, rational limits for temperature and relative humidity can be calculated in order to ensure the total physical safety of the photographic materials.

The material properties research has also shown that old "embrittled" materials have the same or even greater degree of elasticity (due to strain hardening effects). However, they often lose the ability to plastically deform compared to new materials so breakage occurs more readily. Hence, we perceive old materials as more delicate to handle safely, and this is true because any deviation outside the elastic regime more easily causes breakage. Nonetheless, the allowable environmental cycle which keeps the aged and embrittled material within the elastic regime is the same or greater than when the material was new. To summarize, environmental fluctuations that do not cause the materials to exceed their yield point, whether they occur seasonally, daily, or hourly, will induce only expansions and contractions that are totally reversible, and physical stability is ensured. Photographic films or papers will respond to the environmental cycle by changing dimension and degree of curl, but in a reversible fashion that does not cause permanent deformation or fracture.

Chemical and Physical Stability:

From the preceding discussion, it is clear that allowable ranges of temperature and relative humidity must incorporate knowledge of both the chemical stability and physical stability. Because the photographic materials considered in this paper contain gelatin and very often other hygroscopic materials as well, the relationship between moisture content within the photographic material and the material's physical and chemical stability is very important.

The Moisture Content Equilibrium State in Photographic Materials:

Photographic materials are very hygroscopic in nature. Even when films and papers are "dry" they hold significant quantities of water absorbed within the molecular structure. The moisture content of the gelatin layers are of particular significance. For example, at 22°C and 50% RH, gelatin contains nearly 14% by weight of water. At 22°C and 80%RH (above T_g) the gelatin contains approximately 20% by weight of water. Moisture content is a vital parameter relating to the chemical and physical stability of photographic materials, but it is not conveniently measurable, and relative humidity has largely come to be viewed as an equally

meaningful indicator. While the moisture content of gelatin and other hygroscopic materials like paper or triacetate film base is indeed related to relative humidity under environmental equilibrium conditions, the equilibrium state is also influenced by temperature and pressure as well. Generally, pressure can be treated as a constant value (standard atmospheric pressure), but the influence of temperature cannot be overlooked if environmental guidelines for storage and use allow large excursions from ordinary room temperature. The relationship between temperature, relative humidity, and moisture content in photographic gelatin at standard atmospheric pressure has recently been investigated.¹⁸ It is not a simple unvarying relationship, but a useful generalization can be made. In order to maintain a constant level of moisture content within the gelatin emulsion the relative humidity must be reduced by 3-4% RH for every 10°C drop in temperature. It follows that maintaining a constant relative humidity set point as temperature is lowered will lead to additional water absorption within the gelatin layers. Other hygroscopic polymers such as cellulosic materials and acetate film supports display similar behavior. This physical behavior has important implications for cold storage of photographic materials which will be addressed in more detail later in this paper. However, proper compensation for the effect is achieved by incorporating gradually decreasing RH levels into the environmental guidelines as the temperature level at which the photographic materials are kept is reduced.

The Importance of the Glass Transition Temperature of Gelatin:

The glass transition of gelatin is essential to the very existence of modern photography and is also of great significance to the preservation of photographs. Material scientists define the glass transition temperature of a material as a discontinuity in the rate of change of specific volume with respect to the change in temperature. In practical terms, gelatin's glass transition is easily recognized by changes in physical handling characteristics. Below a critical glass transition temperature (T_g), gelatin is a hard, tough polymer. Above T_g , gelatin becomes "soft and rubber-like" to the touch. The gelatin changes from a solid state to a gel state. This distinctive change in material properties is not as sharply defined as the melting point of a crystal (e.g., ice to water) but is discreet enough for a specific temperature value to be assigned to the transition. Hygroscopic polymers like gelatin have an interesting and very important additional feature, i.e., T_g changes significantly with moisture content. The higher the moisture content of the gelatin the lower the temperature needed to make the gelatin change from the solid to the gel state. This behavior is what makes gelatin uniquely suited to photography. When water is used to wet the gelatin emulsion the moisture content increases dramatically, and the glass transition is now crossed at a temperature value below ordinary room temperature. Photographic processing then becomes possible. Above T_g , the gelatin is highly permeable and allows chemical agents to rapidly diffuse through the gelatin and reach the silver halide crystals.

Unfortunately, gelatin does not have to be fully wet by liquid contact in order to reach the gel state at room temperature. Very dry gelatin has a T_g value above 200°C, but T_g drops to room temperature (22°C) when the gelatin has equilibrated to a relative humidity condition of approximately 70 to 75% RH. At 30°C, gelatin needs only to be in equilibrium at approximately

65% RH. The hard, dry, protective properties of the gelatin coating disappear and are replaced by the highly permeable gel state properties. Thus, photographic emulsion layers are very sensitive to environmental conditions which often occur in the real world. The low glass transition temperature of gelatin at high RH is a fundamental reason why high humidity is so detrimental to photographs. Emulsions which stick together and to other objects, changes in emulsion surface appearance (ferrotyping), and serious mould damage are direct consequences of gelatin stored above its glass transition temperature. The oxidation-reduction process on silver image particles which causes the appearance of "silver mirroring" is also promoted by gelatin in the gel state. Silver ions can diffuse away from the original silver site more readily because the diffusion rate is much higher when the gelatin binder layer is functioning in the gel state rather than in the solid state. With regard to proper environmental storage after a photograph has been properly processed and dried, it is extremely important to avoid environmental conditions that will cause the gelatin to cross its glass transition and revert to the gel state.

The Dominant Role of Temperature on Chemical Stability:

High relative humidity is clearly a critical parameter when it causes the gelatin to exceed T_g under normal use or storage conditions. Additionally, high-to-low relative humidity cycles lead to high mechanical stresses that cause permanent plastic deformation, and eventually cracking or delamination of the coating layers. Thus, for reasons of both chemical and physical safety the practical range of relative humidity at ordinary room temperature levels must be confined to within moderate limits, approximately 35-60% RH. Changes in RH within this humidity range can affect the chemical stability of photographs by a factor of two or three. Similarly, limits for temperature can be established. Conventional photographic materials are physically tolerant of wide temperature changes, so the limits primarily reflect considerations of chemical stability. Temperatures above 25°C can be ruled out simply because chemical stability is compromised too much. Temperatures lower than -25°C are not useful because further gains in chemical stability cannot be realized in practice. The time a photograph spends out of cold storage and in use at room temperature ultimately limits the overall level of chemical stability, no matter how stable the materials are in storage.¹⁷ The influence of "time out of storage" will be addressed in a following section of this paper.

Within the temperature range from 25°C to -25°C reductions in temperature can slow aging rates more than 100-fold. Since many photographic materials will suffer serious levels of deterioration in less than a century under room temperature keeping conditions, the dramatic improvement in chemical stability afforded by low temperature storage is essential for the long term preservation of photographic materials. Although low temperature storage imposes practical constraints in terms of access to the collection, the importance of preservation must outweigh the restrictions on immediate use for photographic collections having permanent historical value.

The Allowable Range of Temperature and Relative Humidity:

Based on the preceding discussion of chemical and physical stability, the allowable combinations of temperature and relative humidity can be plotted graphically as shown in figure 1. Region #1 shown in figure 1 represents the combinations of temperature and relative humidity which are both chemically and physically safe for conventional photographic materials (i.e., films, plates, and papers with gelatin emulsions). Points A, B, C, and D delineate the boundary conditions for region #1, and as long as the photographic materials remain in equilibrium anywhere within this region, an inherent degree of physical and chemical safety is ensured. Region #1 also compensates for the relationship between gelatin's moisture content and relative humidity as temperature is decreased. Moreover, any combination of relative humidity and temperature located within region #1 can be invoked at any time. There are no limitations on the frequency or magnitude of the environmental change as long as the change does not fall outside region #1. In other words, one may cool or warm, desiccate or humidify, or combine any amount of humidity and temperature change with complete freedom as long as the photographic materials are not subjected to excursions outside region #1. In order to remain within region #1 cold objects must be warmed with care, otherwise temporary deviations caused by temperature induced moisture gradients and dewpoint conditions may occur. Often, a simple vapor barrier provides adequate protection from direct condensation. Also, it is important to note that cold materials can lose a significant amount of their ability to plastically deform, so any additional mechanical stresses applied to them over and above the allowed environmental stresses may cause cracks or breakage. Careful handling and packaging which prevents direct bending and flexing of the photographic materials is therefore highly recommended when working with photographic materials in cold temperature storage.

Environmental fluctuations within region #1 are physically safe because they only cause expansions or contractions of the photographic materials that are elastic and reversible. For example, photographs which have contracted or curled slightly due to a change in temperature and RH from 20°C/55% RH to 5°C/30% RH can be reversibly expanded (uncurled) simply by returning once again to 20°C/55% RH. These elastic dimensional changes may be judged by some people to have subtle aesthetic implications, but the changes are not permanent. The perceived differences in appearance are a matter of preference not risk. Region #2 indicates the combinations of temperature and relative humidity that will cause gelatin to exceed its glass transition temperature. Photographic materials will not retain high quality very long under these conditions. The dashed line representing the threshold for T_g in figure 1 has been plotted using data for glass transition available at this time.^{18,19} Some small refinements may be useful in the future as T_g is probably affected to some degree by chemical hardeners, humectants, and other additives that might influence moisture content of the gelatin. However, the temperature and relative humidity combinations identified as region #2 should serve as a reasonable approximation for most photographic emulsions.

Regions #3 and #4 have been added to the graph in Figure 2. These regions represent combinations of temperature and relative humidity that are actually safe for photographic materials with regard to chemical stability, but not totally safe with respect to physical safety. In particular, region #3 leads to a level of chemical safety that is higher overall than region #1, the

primary recommendation. Unfortunately, in order to move into regions #3 and #4 and then return at later times to environments within region #1, photographic materials may experience a full environmental cycle that causes some plastic deformation to occur. Plastic deformation may be unavoidable at times because rigorously staying within the boundaries of region #1 may not always be possible. However, it is important to realize that an environmental guideline which seeks to avoid any plastic deformation (by staying within region #1) is very conservative. Plastic deformation often does not cause visually detectable problems, and photographs are manufactured to withstand considerable amounts of such treatment. For example, the act of wet processing causes one cycle of plastic deformation since the wet emulsion must pass through extremes in region #2 before it reaches an equilibrium dry state preferably within region #1. Print flattening by heat and/or pressure is another example of deliberate plastic deformation. Thus, photographic materials can generally tolerate a significant amount of this kind of physical cycling, but their inherent physical stability cannot be guaranteed. Hence, excursions outside region #1 are to be avoided. Such excursions may lead to physical damage sooner or later depending on the type and age of the materials and the frequency and magnitude of the excursions.

Because chemical stability increases as temperature and relative humidity are decreased, some conditions within region #1 render more chemical stability than others even though region #1 was selected to provide at least a minimum level of chemical stability and the full measure of physical stability. As indicated in figure 3, the chemical stability in region #1 increases as the chosen environment is shifted from point B (least chemically stable) to point D (most chemically stable). The relative chemical stability factor corresponding to each contour line was calculated from Arrhenius test data on the dark fading characteristics of typical chromogenic color dyes.²⁰ The relative stability has been normalized in figure 3 to a value equal to 1.0 for a standardized museum environment at 21°C/ 50% RH. Although these contour lines were derived from chromogenic dye stability data, they serve as a general guide to illustrate how different combinations of temperature and relative humidity affect the chemical stability of photographic materials. The trend holds true because the activation energy for the dark fading of chromogenic dyes and their response to RH is similar to other important aging mechanisms in photography, notably acetate base degradation. As an example, the coordinates 5°C and 45% RH fall close to the contour line with a value equal to ten. A photograph stored at 5°C/45% RH is about ten times more chemically stable than when it is in use at 21°C/ 50% RH. Although the contour lines are approximations, the trend clearly demonstrates how cool and cold storage improves the longevity of photographic materials. However, the practical value of a specific combination of RH and temperature values depends on a number of considerations besides chemical stability. These considerations include ease of access, human comfort during use of the collection materials, and the cost of constructing and maintaining a particular environment. The collection manager's decision is further complicated by operating costs that are not a simple function of either temperature or humidity.

To summarize, all combinations of temperature and relative humidity located within region #1 have significant value to photographic conservation. The logic behind region #1 is to provide a range of conditions that can be used interchangeably to enhance chemical stability, provide convenient use or display conditions, and simultaneously protect the materials from

physical damage. Clearly, the best way to balance preservation and exhibition needs is by maintaining two distinct but physically safe climates, one to impart superior chemical stability in storage, the other to ensure a reasonable level of chemical stability during use.

Once again, consider what happens to cold stored objects that are to be used at room temperature. They can move safely in the recommended zone as often as is desired. There are no limits to the frequency and magnitude of the environmental changes within this allowable zone. However, failure to keep a vapor barrier in place or to raise the temperature slowly can cause excessive humidity, even water condensation, on a collection object that is initially in cold storage and then removed to a warmer user environment. The microclimate at the surface of the object then deviates from the boundary conditions set by region #1 even if the new display environment to which the object has been transferred is in full compliance with region #1. Care must therefore be taken not to raise temperatures too rapidly. Thermal shock is not the issue. Photographic materials cannot be heated or frozen fast enough under any ordinary circumstances to cause physical damage which can be attributed to thermal shock. The problem of rewarming a cold object is strictly one of making sure that a temperature gradient does not cause moisture migration and condensation. Common sense should prevail when removing photographic materials from cold storage in order to guarantee that the microclimate at the surface of the photographic material is not deviating from the allowable humidity range.

Microclimate Effects in Sealed Packages:

Careful inspection of figure 1 reveals that the allowable RH range for cold temperature storage (e.g., line CD) is slightly narrower and shifts to the left compared to the humidity tolerances at room temperature (e.g., line AB). As discussed previously, a lower RH level must be established at low temperatures in order to retain the same moisture content level which exists in gelatin at room temperature. This is a natural consequence of the way the gelatin equilibrium moisture content changes in response to changes in temperature and relative humidity. The narrowing of the RH range is due to convergence as the RH value draws closer to its limiting value of zero. A humidity controlled cold storage vault complies with the allowable temperature and RH range in a straightforward way. For example, the relative humidity at -25°C can be fixed or allowed to fluctuate anywhere between 20% RH and 40% RH. Objects so stored may be safely returned to room temperature, up to 25°C for example, where their moisture content is now in equilibrium with a specific RH value somewhere within the 35% to 60% RH range denoted by line AB. Because it is assumed that photographic materials which are kept in humidity controlled rooms can "breathe" and thus equilibrate to the surrounding RH level, any changes in moisture content will be safely limited to the environmental boundaries of region #1 provided that storage and user environments comply with the temperature and humidity values established by region #1. But what about sealed or quasi-sealed packages that don't allow the object to easily equilibrate to the surrounding environment? Very few photographic materials are actually stored as individual items on a shelf. Most photographic materials are housed in envelopes or packages and further packed with other items in larger boxes or containers. Practically speaking, very few photographs are truly allowed to "breathe".

The container or package that houses them isolates the climate inside the box from the conditions of the surrounding environment. An important microclimate is thus established inside the box for extended periods of time before moisture equilibration with the surrounding environment can occur. While temperature equilibrium may be reached in hours, moisture content equilibrium may take days, months, or even years to be reached, especially at cold temperatures where diffusion rates of water vapor are significantly lower. The typical package of photographic materials is usually moderately or densely packed with photographic items. Consequently, little free air volume exists compared to the amount of materials inside the package, and the microclimate inside the package is actually "over buffered" by the moisture absorption capacity of the photographic materials.¹⁸ Because the moisture content inside the package remains essentially constant for long periods of time, the RH inside the sealed package automatically shifts within a matter of hours in order to maintain the natural equilibrium state which must exist between moisture content, relative humidity, and temperature. This behavior is illustrated in figure #4 by the points H and I. A box of photographic prints sealed at 23°C/58% RH (point H) will follow the environmental path marked by the arrow inside region #1, and at -18°C the microclimate inside the package will stabilize at approximately 40% RH (point I). Upon return to a steady state condition at 23°C the package will again have an internal relative humidity of 58% RH (point H). The correlation of decreasing RH with decreasing temperature is counter-intuitive to many people because they are often familiar with psychrometric charts which show that RH will increase in a volume of air as the temperature is decreased. Psychrometric charts identify the moisture holding properties of air and do not take into account the moisture buffering properties of hygroscopic materials like gelatin, paper, and acetate film base.

A potential risk also arises from the microclimate characteristics of packaged photographs. If a sealed package slowly equilibrates over time to a surrounding environment outside of region #1, it drifts out of compliance with the recommended range. Consider line JK in figure 4. At point J, the -18°C/65% RH level is an environment typical of conventional freezers. If a high moisture barrier package was stored in a conventional freezer with an initial microclimate at point I, but the package leaked slowly over time, it would eventually come to equilibrium at point J. This new microclimate is still very safe for the object in terms of chemical stability as can be inferred from the contour lines in figure 3. However, upon warming to room temperature the packaging material keeps the extra moisture trapped inside, and the package warms to point K (approximately 23°C/78% RH). Once the glass transition temperature is exceeded, the gelatin's ability to over buffer the package disappears. It now behaves more like a saturated salt solution attempting to properly buffer the environment. Hence, the path denoted by the arrow connecting points J and K takes a slight bend as the glass transition is crossed. The final equilibrium RH will depend, of course, on the proportion of gelatin to the proportion of other hygroscopic materials located in the package, but the general trend illustrated by the path between points J and K is valid. The room temperature condition at point K is risky for both mould damage and emulsion blocking because it is above T_g . This risk can be removed by ventilating the materials as soon as possible after warm-up. Nevertheless, one plastic deformation cycle has now happened, and it is better to avoid this type of excursion altogether.

Time out of Storage:

The contour lines in figure 3 show the remarkable influence of temperature on the life of photographic materials under steady-state conditions. However, the practical benefits of cold storage environments are ultimately limited by the combined effects of storage and use. When photographs are removed from cool or cold environments and then used at ordinary room temperature, the aging rate returns to the rate established by the temperature and relative humidity levels in the user environment.¹⁷ The chemical kinetics of the storage and user environments must be proportionately weighted to account for the amount of time that a photograph spends in each environment. A precise integration would sum up the effects over discreet time intervals at every temperature and RH value encountered. A simpler but very instructive evaluation can be made by assuming just two steady-state environments, one for the user condition and one for the storage area. This evaluation is reported in Table I. The values listed in Table I indicate the effective chemical stability that can be realized after the stability in storage has been compensated for the time that an object is out of storage and in use. Table I assumes that the relative stability is equal to 1.0 when the object is in use. As in the contour lines in figure 3, a relative stability value equal to 1.0 is obtained at 21°C/50% RH or other comparable environment. "Time out of storage" is treated as an amortized amount of time, i.e., an average number of days per year that an object is out of the storage vault and in use. For example, a color print that has been exhibited for six months at room temperature after spending 20 years in cold storage has spent approximately 9 days per year out of storage. Table I demonstrates that as the chemical stability in the storage area improves, the time out of storage becomes increasingly more influential. For example, in Table I, row 2, the chemical stability of the storage environment is identical to the user environment, so the time out of storage has no effect. In row 1, the storage environment is worse than the user environment so the relative chemical stability actually increases as the materials spend more and more time in the user environment. A very stable storage environment is shown in Row 8. The materials are 500 times more stable in storage than on display. However, small amounts of time out of storage now dramatically affect the overall level of chemical stability that can be achieved in practice. If a photograph is removed from this exceedingly stable storage environment and returned to room temperature use at 21°C/50% RH for 1, 2, 5, 10, or 30 days per year out of storage, the relative chemical stability drops to 211, 134, 64, 34, and 12, respectively.

Table II illustrates the contrasting nature of the RH and the time-out-of-storage parameters. At temperature levels close to ordinary room temperature the relative humidity in the storage area is important while the time-out-of storage parameter is insignificant. For example, cool storage at 15°C and 56% RH approximately doubles the chemical stability compared to the museum standard condition of 21°C/50% RH. Reducing the RH in the storage area to 32%, the lowest allowable, increases the relative stability even further to a value of 4. Under these conditions, table II shows that up to 30 days per year out of storage does not seriously alter the effectiveness of the cool, low RH storage environment. On the other hand, at low storage temperatures the time-out-of storage parameter is more important than RH. Consider the highest and lowest allowable RH values in freezer storage. Five days per year out

of $-20^{\circ}\text{C}/21\%$ RH storage yields an effective relative stability value of 66 while the same time out of $-20^{\circ}\text{C}/42\%$ RH storage yields a value of 61. For low temperature storage, the time-out-of-storage parameter dominates. RH has now become irrelevant with respect to chemical stability and is essential only for physical stability:

Although it is perhaps surprising to see how much stability is given up with even small amounts of time out of storage, low temperature storage is still far more effective in preserving a photographic collection than room temperature storage at low RH. The collection manager must carefully choose how much time materials spend outside of the storage vault. If an object is always out of cold storage, no chemical stability benefit can accrue. On the other hand, if an object is never allowed to leave cold storage, any useful purpose for the collection seems unlikely. Cold storage is a vital preservation strategy, but it must be complemented by careful planning for exhibition, handling, and scholarly use.

Summary and Conclusions:

Several concepts have been discussed in this paper which are interrelated and contribute to the overall physical and chemical stability of conventional photographic materials. An understanding of these concepts led to the allowable range of temperature and relative humidity which is shown in figure 1. The recommendations and the underlying concepts are incorporated in figure 1 and also reflect a basic collection management strategy. This strategy can be summarized as follows.

- 1). *Lower temperatures and to a lesser extent lower relative humidity levels increase chemical stability. Maximum chemical stability is achieved at sub-zero temperatures (-20 to -25°C).*
- 2). *Low temperature storage is essential for the long-term preservation of photographic collections because most photographic materials do not possess enough inherent chemical stability to survive in good condition for decades at ordinary room temperature.*
- 3). *The optimum way to preserve photographic materials is to maintain two distinct but physically safe climates, one to impart superior chemical stability in storage, the other to ensure a reasonable level of chemical stability during use or exhibition. Careful management of the time spent on exhibition versus time in storage is crucial to this approach.*
- 4). *The safe upper limit for use and display of photographic materials is approximately 25°C at 60% RH. Physical safety is ensured between 35% and 60% RH at 25°C .*
- 5). *Keep processed photographic materials below the glass transition temperature of gelatin at all times.*
- 6). *As temperature is reduced, the relative humidity set point in the storage area should be adjusted downward to compensate for the moisture absorption capacity of the gelatin (i.e., by*

reducing the RH approximately 3-4% RH per 10°C drop in temperature). The relative humidity within sealed packages adjusts automatically due to the moisture buffering properties of the photographic materials inside the package provided that the package does not contain excessive free air volume.

7). Cold photographic materials should be warmed slowly and moisture vapor barriers used if necessary in order to avoid transient high humidity conditions and water condensation problems at the photographic emulsion's surface.

8). Cold stored films, papers, and plates must be handled with great care because any mechanical forces that exceed the elastic limits are more likely to cause brittle fracture.

The temperature and relative humidity recommendations in this paper consider both chemical and physical stability to safely exhibit and store photographic materials. Conservative scientific protocols were used to establish limits of physical safety. The great majority of conventional photographic films and papers use gelatin as the image binder layer coated on a limited variety of base materials, i.e, glass, polyester, paper, resin-coated paper, and cellulose acetate supports. For these photographic media, all set points and environmental fluctuations that occur within the ranges defined by region #1 in figure 1 are permissible. The frequency and magnitude of the changes within this region do not contribute to any physical damage. Thus, the recommendations are flexible, particularly in regard to mixed media collections. Two basic environments are necessary, one for storage and one for use. The desired chemical stability is established by selecting and managing these two environments. Lower temperature in the storage environment is critical for preservation purposes because the chemical stability benefits derived from low temperatures cannot be obtained during room temperature use or exhibition. A suitable storage environment can be determined by estimating the likely amount of time out of storage, selecting the desired level of effective chemical stability from Table I, and identifying the corresponding storage parameters required to meet the goal from figure 3. Choosing the appropriate level of chemical stability clearly depends on other issues as well. These include but are probably not limited to ease of access, type and existing condition of the collection materials, and the costs of constructing and operating the necessary storage and display environments.

Most existing storage standards published to date recommend conditions that typically fall somewhere within the allowable range shown in region #1. Some standards have exploited part of region #3. Region #3 is chemically very safe but may lead to physical problems over time caused by accumulated damage from plastic deformation as objects move to and from conditions of storage and normal use.

The allowable environmental range and fluctuations give the collection manager latitude to develop a sensible preservation plan for photographic collections. Nonetheless, the recommended range is not sufficiently wide enough to eliminate the need for humidity and temperature control. Without some type of mechanical controls, many regions of the world will not be able to achieve full compliance for a safe exhibition environment, and the tremendous advantages of low temperature storage will be missed.

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Region #1: Chemically and Physically Safe
 Region #2: High Risk because Gelatin crosses T_g

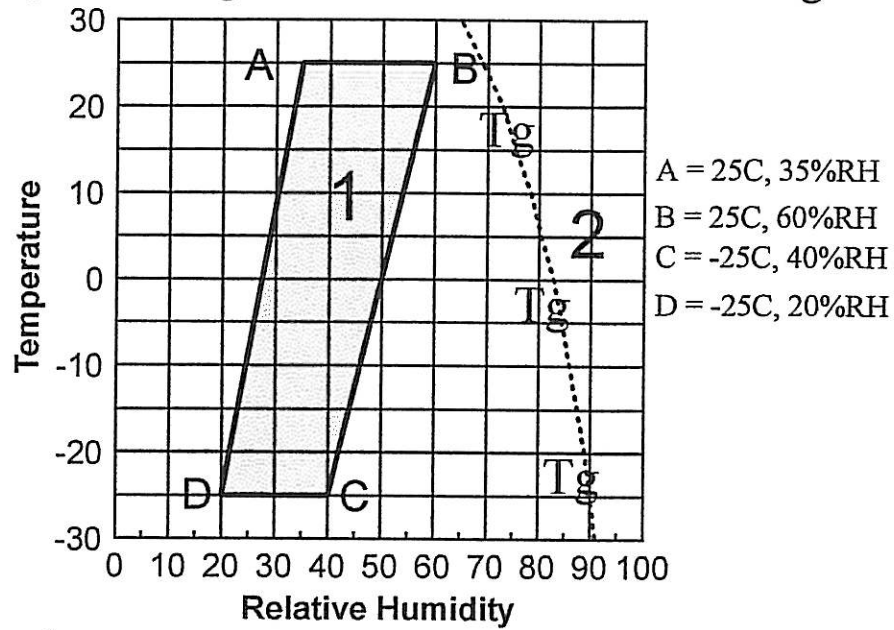


Figure 1.

Regions #3 and #4: Chemically Safe but not Physically Safe

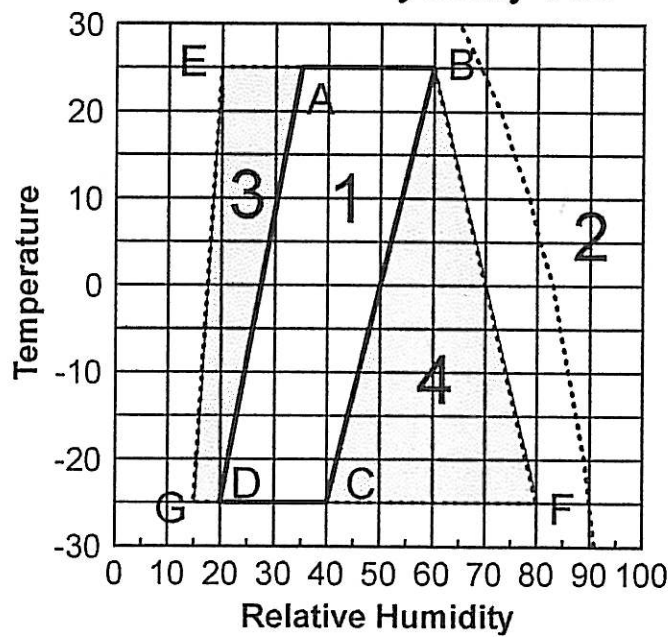


Figure 2.

Contour Lines of Equivalent Chemical Stability

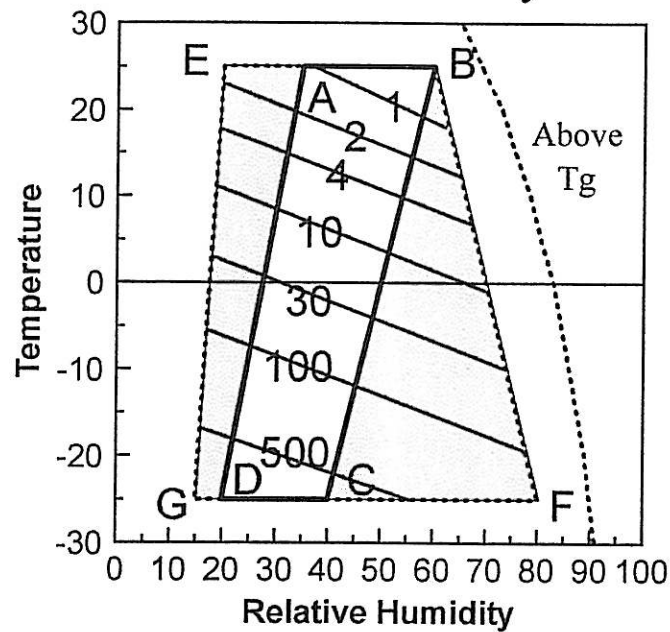


Figure 3.

Microclimate Response of Confined Photographic Films and Papers

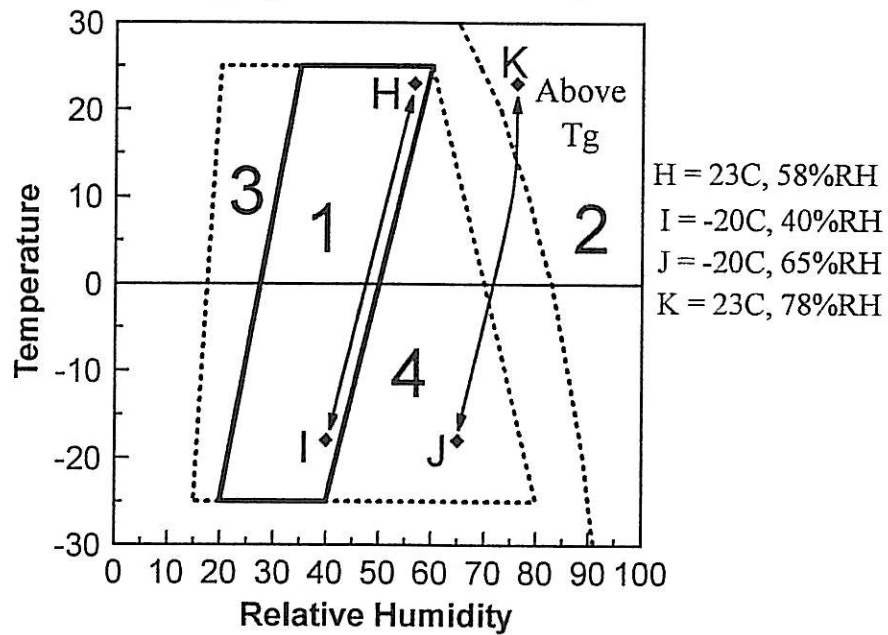


Figure 4.

Table I
Relative Chemical Stability Values Compensated for
"Time out of Storage"

Relative Chemical Stability in Storage	Time out of Storage (Days per Year).....								
	0	1	2	5	10	30	60	180	365
	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.7	1.0
	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	2.0	2.0	2.0	2.0	1.9	1.8	1.7	1.3	1.0
	4.0	4.0	4.0	3.9	3.8	3.7	3.2	2.7	1.0
	10	10	10	9	8	6	4	2	1
	30	30	28	26	21	17	9	5	2
	100	100	79	65	42	27	11	6	2
	500	500	211	134	64	34	12	6	2
	1000	1000	268	154	68	35	12	6	2

Note: Relative chemical stability of display environment normalized to 1.0

Table II
Combined Effects of Temperature, Relative Humidity, and
"Time out of Storage" on Chemical Stability.

Storage	Temp	RH	Time out of Storage (Days per Year)				
			0	2	5	10	30
Museum standard	21	50	1.0	1.0	1.0	1.0	1.0
Cool, High RH	15	56	1.9	1.9	1.9	1.8	1.8
Cool, Low RH	15	32	4.1	4.0	3.9	3.8	3.3
Cold, High RH	5	52	9	8	8	7	5
Cold, Low RH	5	28	18	16	15	12	8
Freezer, High RH	-20	42	380	124	61	33	12
Freezer, Low RH	-20	21	690	145	66	35	12

Note: Relative chemical stability of display environment normalized to 1.0